

Electronic Supplementary Information

Photocatalytic reduction of nitro-aromatic compounds: Selectivity control through reaction space control

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Table of Contents

- 1 Materials & Methods
 - 1.1 Materials
 - 1.2 Characterization
 - 1.3 Experimental procedures
- 2 Continuous-flow microreactor experiments
- 3 Spectral data of products
- 4 References

1 Materials & Methods

1.1 Materials

In general, all chemicals were used as purchased without further purification. Eosin Y, Nitrobenzene, 4-Nitrotoluene, 4-Nitrobenzonitrile (97%) were purchased from Sigma-Aldrich (Korea). Nitrosobenzene was purchased from TCI (Korea). Triethanolamine (TEOA), 4'-Nitroacetophenone (98%), 1-Chloro-4-nitrobenzene (98+%), 4-Nitroanisole were purchased from Alfa-Aesar. 1-Bromo-4-nitrobenzene was purchased from Acros organics. Water, Ethyl Alcohol (EtOH), dimethyl sulfoxide (DMSO), Hydrochloric acid (HCl) (37%) were purchased from Samchun Chemicals (Korea). Green LEDs (60 mW, $\lambda=520$ nm) were purchased from Jinledmart (Korea) and soldered by ourselves. High transparent perfluoroalkoxy alkane (HPFA) tubing (ID: 1 mm and 500 μ m) was purchased from IDEX HEALTH & SCIENCE (WA, USA). KD Scientific Legato 180 syringe pump (Holliston, MA, USA) was used for continuous-flow reaction.

1.2 Characterization

The products were detected by GC-MS (Agilent Technology, 7890A-5975C with Triple-Axis detector) and by Nuclear magnetic resonance (NMR) (Bruker Avance III, 500 MHz for ^1H -NMR). ^1H chemical shift were recorded in ppm downfield of Me_4Si or CHCl_3 as a standard in CDCl_3 unless otherwise noted. UV-vis spectra were recorded using 10 mm quartz cuvette by NANODROP 2000c spectrophotometer (Thermo Scientific).

1.3 Experimental procedures

Basic procedure for photocatalytic reduction of nitrobenzene (NB) was followed by modified previous work.¹ Briefly, 0.4 mmol of NB (or *para* substituted nitro-aromatic compounds) was dissolved in 10 mL of water and ethanol mixture (2:3 vol. ratio). Then, 6 equivalents of triethanolamine (TEOA) and 1 mol% of Eosin Y were added in the solution. The pH of the solution was adjusted to 8.5 by adding a few drops of HCl. The solution mixture was degassed under vacuum and filled with Ar (3 times). Then the solution was purged by bubbling Ar for 30 min. For continuous-flow reaction, the deaerated mixture was finally transferred to 10 mL syringe and infused by syringe pump.

For the light irradiation set-up, octagonal box was prepared and mirrors were attached to inside wall for light reflection. (Figure S1) The green LEDs (16 ea) were surrounded inside of box. Small fan was used to get rid of heat from the light source during the reaction.

After reaction, the products were extracted by chloroform (3 x 20 mL) from the mixture. The extracted organic phase was washed with 5% sodium bicarbonate (3 x 20 mL) and brine solution (3 x 20 mL). Water was removed from organic phase using anhydrous sodium sulfate and the organic phase were concentrated *in vacuo*. The products were identified by GC-MS spectrometer and ^1H -NMR.

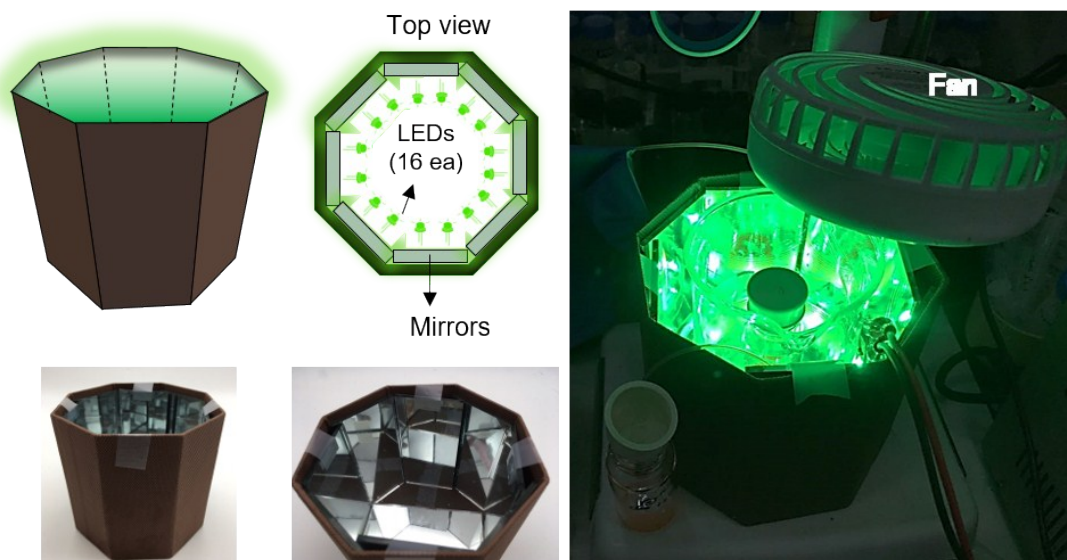


Figure S1. Schemes and images of photoreaction set-up for batch reaction and continuous-flow reaction.

2 Continuous-flow microreactor experiments

2.1 Fabrication of parylene film microreactor

The parylene film microreactor was fabricated by thermal bonding of two parylene layers. (Figure S2) The microchannel which has a cross-sectional dimension of $500\ \mu\text{m} \times 110\ \mu\text{m}$ (width \times height) was patterned by deep reactive-ion-etch (DRIE) process on the bare silicon wafer. The patterned silicon substrates were dipped into piranha solution (95% of H_2SO_4 : 35.5% of H_2O_2 = 2:1) at 130°C for 8 h, prior to next steps. The surface of silicon wafer was treated by Tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS, Gelest, USA) which helps parylene layer easy detachment from the substrates after bonding process. For FOTS surface treatment, both silicon wafers and two vials filled with an equal amount of FOTS and DI water individually were placed inside a desiccator to maintain a constant vapor partial pressure of each molecule. The cleaned substrates, then reacted with FOTS inside the desiccator for 1 h 30 min at 70 Torr. After surface treatment between vaporized FOTS molecules and hydroxyl groups on the silicon substrates, the substrates were annealed inside a 120°C vacuum oven (350 Vacuum Drying Oven, Samheung, Korea) for 1 h to strengthen the adhesion between FOTS molecules.² After surface modification, the parylene layers were deposited using chemical vapor deposition (SCS Labcoater 2, Specialty coating system, USA) at room temperature to produce uniform and conformal films with controllable thickness. In this study, $\sim 20\ \text{g}$ of Parylene C dimer (DIMER DPX C, Specialty coating system, USA) was used to form $\sim 10\ \mu\text{m}$ thickness parylene film on the substrates.

To bond the parylene layers on each side of the substrates, conventional parylene/parylene thermal bonding method was used. The substrates were bonded under pressure using a custom-built compressor at an elevated temperature of 180°C for 8 h. A vacuum oven was used to remove air bubbles that may be trapped between the substrates and to remove oxygen to avoid oxidation damage to parylene. After degassing all the oxygen inside the vacuum oven for 15 min, nitrogen was filled inside the oven. Thermally bonded thin parylene microchannels were gently peeled off from the substrates then placed on the polyethylene terephthalate (PET) film ($100\ \mu\text{m}$ thickness) covered with thin layer of UV glue. Placing additional PET film underneath the thin film parylene microchannel allows easy handling of the entire device. For inlet and outlet connection, diced glass slides with holes ($\sim 2\ \text{mm}$) was aligned and bonded using UV glue. To open inlet and outlet, only the top layer of parylene channel were precisely removed using a laser cutter (Universal VLS3.50, Universal Laser Systems, USA)

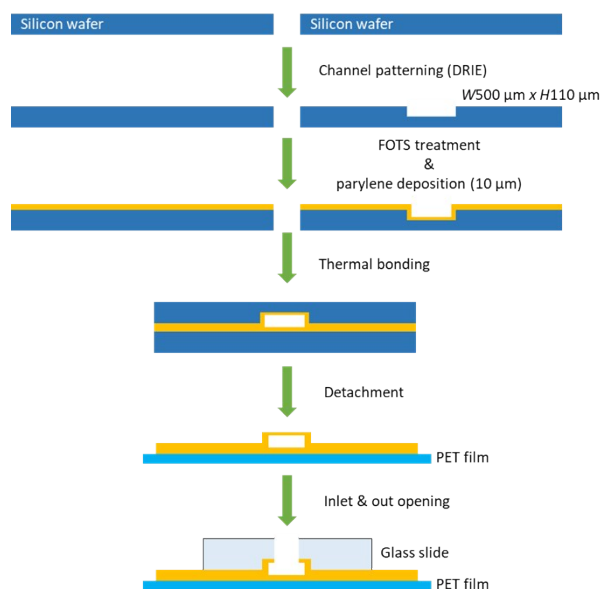


Figure S2. Scheme of fabrication process for parylene film microreactor.

As fabricated parylene film was assembled with metal holders to connect inlet and outlet interfaces. **(Figure S3b)**³ The reactor was placed on the green LEDs plate (60 mW, 16 ea). Note that we used same power of LEDs and only changed the position of LEDs from circular type **(Figure S1)** to planar type **(Figure S3c)**. The solution was introduced to parylene film microreactor using syringe pump. Small fan was used to get rid of heat from the light source during the reaction. The remaining work-up process was same with experimental section 1.3

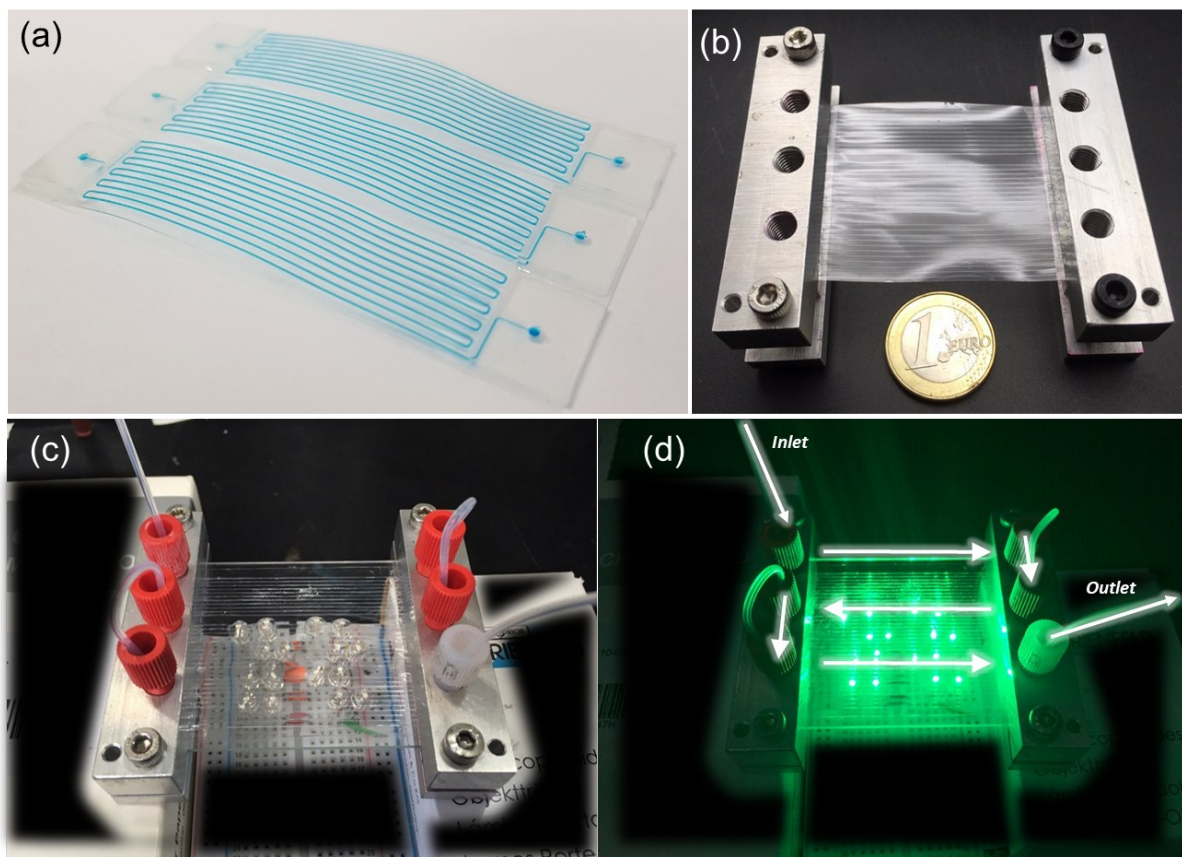


Figure S3. (a) The thin and flexible parylene film reactor with blue dye, (b) the film reactor assembled with metal holder, (c) the tubing connected reactor on the LEDs, (d) the reactor in presence of light and flow directions.

Table S1. Photoreduction of nitrobenzene with various size of CFMs.^[a]

Reactor size	Time	Conversion [%]	Yield [%]		
			NSB	AN	AzxB
ID ^[b] : 1 mm (capillary)	100 min	66.5	0	0.7	65.8
ID: 500 μ m (capillary)	100 min	98.5	0.5	0.5	97.5
H ^[c] : 100 μ m (parylene)	50 min	99.1	0	0.5	98.5

[a] Reaction conditions: Nitrobenzene (0.4 mmol), Eosin Y (1 mol%), EtOH (6 mL), H₂O (4 mL), TEOA (6 equiv.), pH 8.5, Green LEDs (520 nm), Room temperature. Conversion and yield were calculated by GC-MS. [b] ID: inner diameter of HPFA (high purity perfluoroalkoxy) capillary microreactor, [c] H: channel height of parylene film microreactor.

Table S2. Calculation of reaction productivity on the various CFMs^[a]

$$\text{Productivity} = \text{Conc. of NB} \times \text{Flow rate} \times \text{Yield}$$

Reactor dimension (type)	Inner volume	Reaction time (flow rate)	Yield (%)	Productivity (nmol/h) ^[b]
ID: 1 mm, L: 5 m (capillary)	~ 4 mL	100 min (40 μ L/min)	65.8	63.2
ID: 500 μ m, L: 8 m (capillary)	~ 1.6 mL	100 min (16 μ L/min)	97.5	37.4
H: 100 μ m, W: 500 μ m, L: 1.8 m (parylene)	~ 90 μ L	50 min (1.8 μ L/min)	98.5	4.26

[a] Reaction conditions: Concentration of NB (40 mM), [b] Productivities were calculated based on the yield of major product (AzxB).

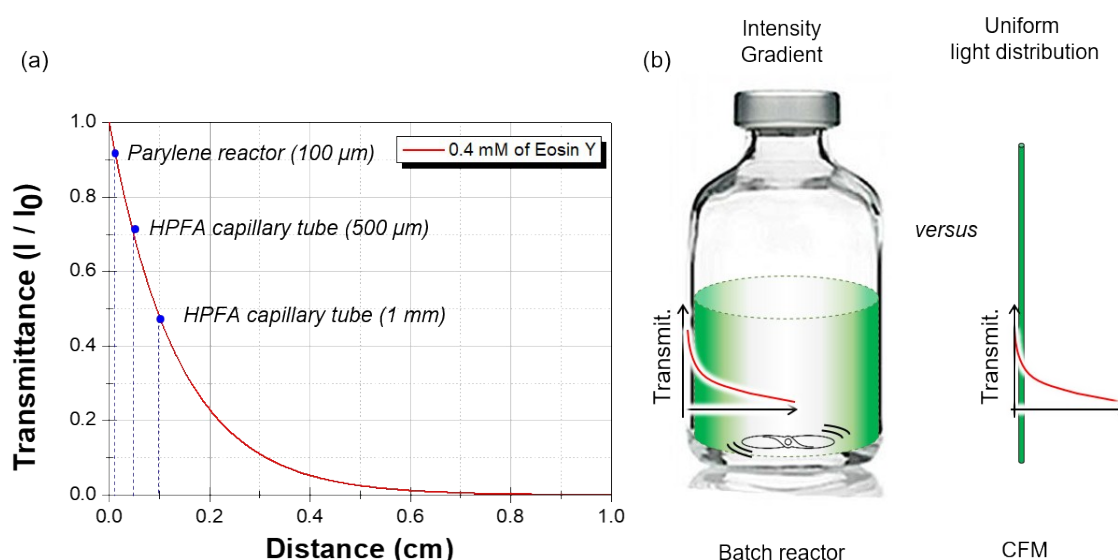


Figure S4. (a) Transmission of light as a function of distance in Eosin Y solution (EtOH/water solvent) (ϵ : 8000 $M^{-1}cm^{-1}$), (b) schematic diagram of transmission of light toward the centre in batch reactor & CFM utilizing the Bouguer-Lambert-Beer correlation.

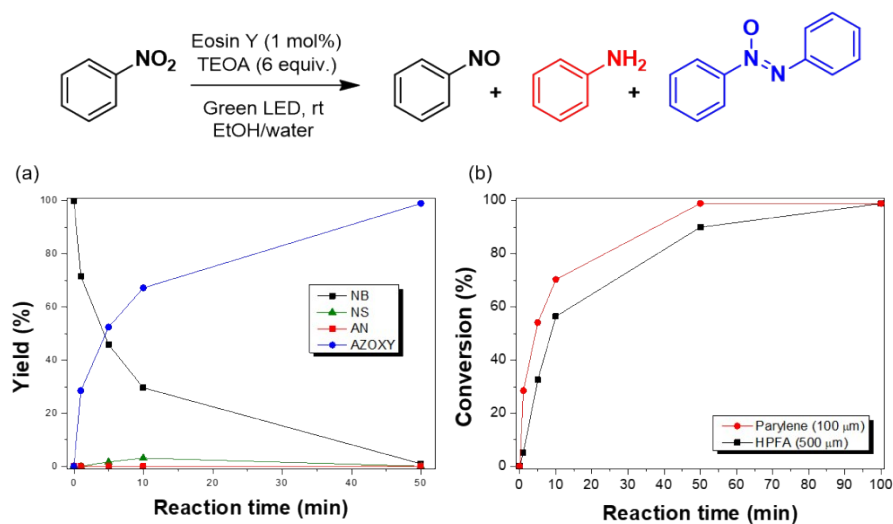


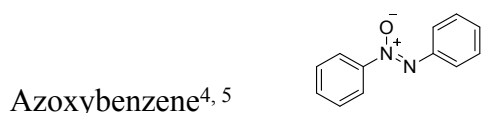
Figure S5. Time-dependent photoreduction of NB (a) in parylene film microreactor and (b) conversion comparison between parylene film (100 μm) and capillary tube (500 μm) microreactor.

Table S2. Photoreduction of nitro-aromatic compounds in CFM with two different substrates.^[a]

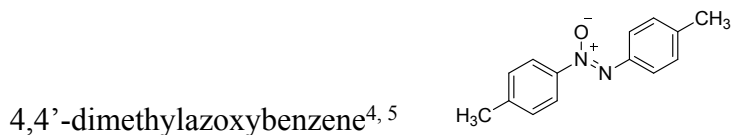
Reactor	Time [min]	Conversion. [%]	Selectivity [%]		
			¹¹ AzxB	¹² AzxB	²² AzxB
R ₁ : H R ₂ : CH ₃	100	98	24	48	26
R ₁ : Cl R ₂ : Br	100	99	24	50	25

[a] Reaction conditions: ID: 500 μm, ¹NB (0.2 mmol), ²NB (0.2 mmol), Eosin Y (1 mol%), EtOH (6 mL), H₂O (4 mL), TEOA (6 equiv.), pH 8.5, Green LEDs (520 nm), Room temperature. Products were detected by GC-MS.

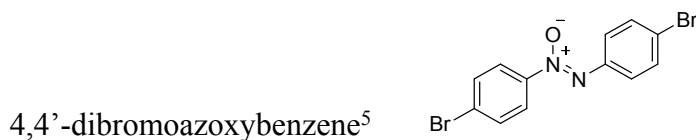
3 Spectral data of products



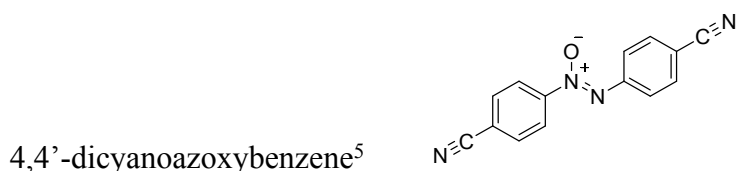
¹H-NMR (500 MHz, CDCl₃) δ 8.25-8.23 (2H, m), 8.10-8.08 (2H, m), 7.50-7.30 (6H, m)



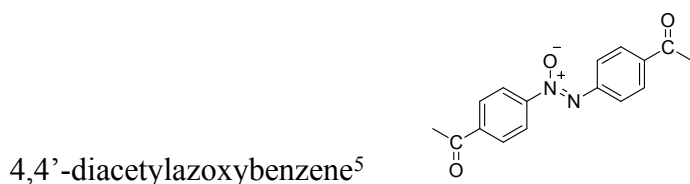
¹H-NMR (500 MHz, CDCl₃) δ 8.11 (2H, d, J= 8.6 Hz), 8.05 (2H, d, J= 7.7 Hz), 7.22-7.20 (4H, m), 2.37 (3H, s), 2.34 (3H, s)



¹H-NMR (500 MHz, CDCl₃) δ 8.11 (2H, d, J= 9 Hz), 8.01 (2H, d, J= 8.9 Hz), 7.57 (2H, d, J= 9 Hz), 7.53 (2H, d, J= 8.8 Hz)

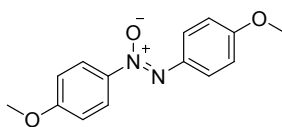


¹H-NMR (500 MHz, CDCl₃) δ 8.49 (2H, d, J=8.7 Hz), 8.25 (2H, d, J=8.7 Hz), 7.89 (2H, d, J=8.9 Hz), 7.82 (2H, d, J=8.7 Hz)



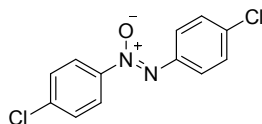
¹H-NMR (500 MHz, CDCl₃) δ 8.45 (2H, d, J=8.6Hz), 8.25 (2H, d, J=8.8 Hz), 8.15-8.10 (4H, dd, J= 8.8 and 8.7 Hz), 2.71 (3H, s), 2.68 (3H, s)

4,4'-dimethoxyazoxybenzene⁴



¹H-NMR (500 MHz, CDCl₃) δ 8.32-8.26 (4H, dd, *J* = 9 and 9.2 Hz), 7.01-6.98 (4H, m), 3.91 (3H, s), 3.90 (3H, s)

4,4'-dichloroazoxybenzene^{4,5}



¹H-NMR (500 MHz, CDCl₃) δ 8.18 (2H, d, *J* = 9 Hz), 8.09 (2H, d, *J* = 9 Hz), 7.41 (2H, d, *J* = 9 Hz), 7.37 (2H, d, *J* = 8.9 Hz)

4 References

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